United States Environmental Protection Agency | Office of Research and Development

National Exposure Research Laboratory
Research Abstract

Government Performance Results Act (GPRA) Goal 1
Annual Performance Measure 231

Significant Research Findings:

Reports on Recommendations for Monitoring Strategy Improvements for States to Use Observations-Based Methods

Scientific Problem and Policy Issues

Ozone is a pollutant of concern because of its adverse effects on ecological and human health. It is well-known that the photochemical system that produces ozone in the atmosphere behaves nonlinearly. This means that estimating the effectiveness of emissions reductions or control strategies, is non-trivial because the ozone response to incremental emission changes depends on a complex balance among chemical precursor species and meteorological conditions. Thus, 3-dimensional air quality models that can account for these factors are needed to develop and evaluate emission control strategies. Since compliance costs are large, we wish to reduce the risk of error providing modeling guidance. We gain confidence in the model through model evaluation, but standard evaluation metrics alone are not sufficient for a nonlinear system. In the ozone system, different combinations of the precursor emissions of volatile organic carbon (VOCs) and nitrogen oxides (NOx) can produce the same ozone. Also, the state of the system can be either VOC-limited, NOx-limited or in between and this cannot be ascertained by simply examining simulated and observed ozone levels. The state of the chemical system is important because when it is VOC-limited, control of VOC emissions is most effective compared to control of NOx emissions. When it is NOx-limited, control of NOx emissions is more effective than control of VOC emissions. Thus, if the air quality model predicts the ozone well for the wrong reason, with the model in the wrong state, then the modeling guidance could be erroneous. The key is that evaluating model predictions of ozone alone cannot determine whether the model is in either the right or wrong state of VOC or NOx limitation. Given the use of the model for policy support, more effective, diagnostic probing is needed to test the photochemical model's representation of the ozone production system and its responses to emission control strategies. The objective of the research is to develop a set of observationally-based indicators of the photochemical processes, termed observationally based methods or OBMs, that involve species that can be or could in the near-future be measured in the field to support not only diagnostic testing of the photochemical models, but also empirical checks on the efficacy of control strategies that have been implemented.

Research Approach

The research approach is to develop special combinations of chemical species from in situ measurements that are capable of probing and testing the photochemical processes in the air quality model. The special combinations of in situ measurements are termed observationally-based indicators. The general approach is termed an OBM approach. This approach supports a special sort of diagnostic model evaluation oriented towards the ozone predictions of the model. The conceptual model of the overall photochemical processing guides the identification of key aspects of photochemical dynamics for which to develop diagnostic indicators. Then process-oriented studies using theoretical constructs, model-derived detailed process-level explanations and results from sensitivity studies with instrumented air quality models (to track the inner workings of the chemistry) are used to develop the indicator probes. The diagnostic or indicator probes are realized in terms of combinations of in situ species or relationships among or between the species. The set of species developed in this analysis also identify species that must be routinely measured in order to carry out OBM studies and to diagnostically test the photochemical models. Comparative studies with model sensitivity analyses are used to identify the most promising and reliable indicators and hence establish the priority set of species to be measured to augment the more routine ozone measurements.

Results and Impact

Diagnostic indicators were developed for three major aspects of the photochemical dynamics. They were air mass aging, ozone production efficiency per NOx termination and the system state relative to the separation line between VOC- and NOx- limitation. A fourth indicator, the competition between termination pathways, developed by researchers outside EPA, was included for analysis. A small set of priority species that supported these indicators was identified. The critical species needed for augmentation of current monitoring are total oxidized nitrogen, or NOy, nitrogen oxide, NO (already available), and an unbaised measure of nitrogen dioxide, or true-NO2. Nitrogen oxide and true-NO2 are combined into an accurate measure of NOx (= NO + true-NO2). Air mass aging is defined as NOy - NOx also termed NOz. Ozone production efficiency is measured by the slope of the relationship between ozone and NOz. And the indicator O3/NOx is informative of the state of the system relative to the line separating NOx- and VOC-limitation. For the competition between termination pathways two (or three) additional species are needed: nitric acid (HNO3) and hydrogen peroxide (H2O2) (or total peroxide). The priority list of species: NOy. True-NO2 (to be combined with NO), HNO3, and H2O2 were communicated to HEASD scientists. The NOy measurement was already available due to development during the

Southern Oxidants Study. HEASD scientists worked with the rest of the list, especially true-NO2, and outside manufacturers to develop methods for the field to be able to measure these species. Significant progress has been made in getting these measurements ready for monitoring programs. With these measurements, we will be able to more effectively test the air quality (photochemical) models with regard to their intended purpose, that is, the prediction of emissions control effectiveness and reduce the uncertainty in and build confidence in model predictions.

Research Collaboration and Research Products	The conceptual model development, theoretical studies, model process instrumentation and the model studies to develop the key set of OBM indicators was conducted by an in house team of NERL scientists and post docs. The NERL team also brought in OBM indicators from university researchers for inclusion and comparison. The key species were communicated to scientists within NERL for instrumentation development. These recommendations have been incorporated into OAQPS planning regarding the new national air monitoring network. The basic, underlying NERL studies are published in: G.S. Tonnesen and R.L. Dennis, Analysis of Radical Propagation Efficiency to Assess Ozone Sensitivity to Hydrocarbons and NO_X. Part 1: Local Indicators of Instantaneous Odd Oxygen Production Sensitivity, *Journal of Geophysical Research*, **105**, 9213-9225, 2000. and G.S. Tonnesen and R.L. Dennis, Analysis of Radical Propagation Efficiency to Assess Ozone Sensitivity to Hydrocarbons and NO_X. Part 2: Long-Lived Species as Indicators of Ozone Concentration Sensitivity, *Journal of Geophysical Research*, **105**, 9227-9241, 2000. Interpretation and explanation of the basic studies leading to measurement recommendations are published in: Arnold, J.R., R.L. Dennis and G.S. Tonnesen, 2003. Diagnostic evaluation of numerical air quality models with specialized ambient observations: testing the Community Multiscale Air Quality modeling system (CMAQ) at selected SOS 95 ground sites, *Atmospheric Environment*, **37**, 1185-1198. and R. L. Dennis, J.R. Arnold, and G.S. Tonnesen. On the need for better ambient observations of important chemical species for air quality model evaluation. W.A. McClenny (Ed.). In *Recommended methods for ambient air monitoring of NO,* NO_2*,* NY_Y*, and individual* NO_Z *species*. EPA/600/R-01/005, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC (2001).
Future Research	No future research with respect to ozone is planned. Diagnostic techniques are being investigated for the inorganic fine particulate system.
Contacts for Additional Information	Questions and inquiries can be directed to Robin L. Dennis, Ph.D. US EPA, Mail Drop E243-01

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